Supporting Information for: Nucleation Effects in the Atomic Layer Deposition of Nickel-Aluminum Oxide Thin Films

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Figure S1: Saturation curves for (a) NiCp₂ with saturating pulse of O₃ and (b) O₃ with saturating pulse of NiCp₂. Self-limiting growth was achieved with a growth rate of \sim 3.5 Å/cycle.



Figure S2: Deconvolution used for the (a) Ni $2p_{3/2}$, (b) O 1s and (c) Ni 3p high resolution scans. The Ni $2p_{3/2}$ spectrum was deconvoluted into two major peaks and three satellite peaks at 860.9, 863.7 and 866.2 eV. The peak at 854.0 eV is attributed to NiO and the peak at 855.6 eV is attributable to both NiO, Ni(OH)₂ and Ni³⁺ species. The O 1s spectrum was deconvoluted into three peaks for Ni-O-Ni (529.3 eV), Ni(OH)₂, NiO defects, Ni³⁺(531.1 eV), and water (532.7 eV).

	Interfacial Layer (1supercycle) (Reflection decay, smoothness)		
	Multilayer stack (Repetitions= total supercycles-2) (Captures density & intensity of Bragg peak)		
	Nucleation layer (1 supercycle) (Low frequency feature)		
SiO ₂			
	Substrate (fixed)		
Si			

Figure S3: Illustration of the XRR model used to fit ternary films with high NiO cycle ratios. The Si and SiO_2 layers were used to model the substrate. The next nucleation layer was used to model the first supercycle. The next layer consisted of repeating bilayers which account for the total number of supercycles minus 2. Finally, a top layer was used to model the final supercycle to capture roughness of the deposited film.



Figure S4: (a) Illustration of the supercycle recipe used to probe the effect of ozone dose on the ternary growth. (b) Measured XPS Ni composition as a function of ozone pulse used. (c) XPS spectra of Al 2p/Ni 3p region for 8 nm thick NiO films with varying amounts of ozone exposure (5 s and 100 s) prior to TMA exposure of 15 pulses of 2 s each. No compositional difference was observed.



Figure S5: Measured oxygen atomic fraction, $\frac{O}{Ni+Al+O}$, by XPS as a function of nickel atomic fraction, $\frac{Ni}{Ni+Al+O}$.



Figure S6: Angle-dependent O 1s XP spectra of NiO ALD. The take-off angle is measured between the detector and the surface. The peak near 529.3 eV is assigned to Ni-O-Ni and the peak at near 531.1 eV is attributed to a convolution of Ni(OH)₂ and nickel oxide defect structures. The shoulder at 532.7 eV is assigned to trace water.



Figure S7: Grazing incidence wide angle x-ray scattering of ALD NiO film deposited on Si coupon. Rings observed by 2D detector are attributed to NiO(111), NiO(200) and NiO(220) in order of increasing Q. No preferred orientation was observed.



Figure S8: Lattice parameter of NiO extracted from the NiO(200) peak in GIXRD scans for Ni-Al-O films as a function of nickel cation fraction.



Figure S9: Calculated densities as a function of nickel cation fraction. Densities were calculated from measured XRR scans and XPS compositions.



Figure S10: A comparison of (a) composition and (b) GPC between the experimental data, the original model shown in Figure 1 and a modified model assuming a 10% lower density of NiO and Al₂O₃ species. For the modified model, the original model was used with the added assumption that for intermixed films, the densities of NiO and Al₂O₃ are 90% of the binary ALD NiO and Al₂O₃ densities. The resulting best fit for the modified model produced a k = -0.38. While the absolute value for k differs from the original model, all the conclusions reached in the analysis of the original model remain valid.

Table S1. Tabulated values of metrics used to evaluate performance of perovskite solar cells with different HTL layers. Underlined values indicate improvement over the standard, NiO HTL.

	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
NiO	18.47 ± 0.18	1.000 ± 0.009	66.03 ± 1.00	12.19 ± 0.12
1	18.82 ± 0.09	1.014 ± 0.006	70.50 ± 1.14	13.46 ± 0.25
2	18.84 ± 0.27	0.980 ± 0.016	55.07 ± 3.33	10.17 ± 0.72
3	16.04 ± 1.07	0.939 ± 0.007	22.93 ± 4.42	3.49 ± 0.85



Figure S11: HR-XP scans of the valence band for the depositions used for solar cell testing. The depositions were performed on Si coupons. XP spectra were shifted using the C1s corelevel energy for adventitious carbon, with the C 1s peak center shifted to 284.8 eV. Relative valence band positions can be seen above. Calculated valence band offsets (VBO) between the perovskite and HTL layers are tabulated in Table S2.

	VBO (eV)
NiO	0.60
1	0.49
2	0.34
3	0.19

Table S2. Tabulated values of valence bandoffsets (VBO) between perovskite and HTLlayers.